

CLAIMS

1. A process for modifying the surface of a substrate containing a polymeric material by contacting the surface with a surface modifying agent to bond the surface modifying agent to the surface the process comprising providing a surface modifying agent composition comprising the surface modifying agent and optionally a carrier therefore and subjecting the surface modifying agent composition to a zone of elevated temperature to vaporize the surface modifying agent composition and provide diffuse contact between the modifying agent and the surface of the substrate.
2. A process for modifying the surface of a substrate containing a polymeric material by contacting the surface with a modifying agent to bond the modifying agent to the surface the process comprising providing a solution of the modifying agent in a solvent and subjecting the solution of the modifying agent to a zone of elevated temperature to vaporize the solvent and provide diffuse contact between the modifying agent and the surface of the substrate.
3. A process according to claim 1 wherein the modifying agent composition is heated to a temperature above the boiling point of the composition prior to contacting the modifying agent with the surface of the substrate.
4. A process according to claim 1 wherein the solution of the modifying agent composition is heated to a temperature above the boiling point of the composition on or adjacent the surface of the substrate.
5. A process according to claim 1 wherein modifying agent composition is heated to a temperature sufficient to produce vaporization of the composition and less than the decomposition temperature of the modifying agent.
6. A process according to claim 1 wherein the heating zone provides a temperature of at least 120°C.

7. A process according to claim 1 wherein the heating zone is selected from the group consisting of a flame treatment zone, combustion chamber, combustion product stream thereof and combination thereof.
- 5 8. A process according to claim 1 wherein the heat treatment means includes a chamber for providing combustion within the chamber and wherein the products of combustion are directed onto the surface of the substrate..
- 10 9. A method according to claim 6 wherein the modifying agent is applied to a heating zone selected from a flame or combustion product stream of a combustion chamber.
10. A method according to claim 7 wherein the solution of modifying agent is applied to the exhaust stream of a pulsed combustion burner.
- 15 11. A method according to claim 6 wherein the combustion chamber provides a plurality of flame zones.
12. A process according to claim 6 wherein the combustion chamber provides pulsed combustion.
- 20 13. A process according to claim 6 wherein the heating means comprises a combustion burner comprising said combustion chamber and said combustion burner further comprises an inlet for an oxidizing atmosphere such as air, a combustible gas inlet for feeding combustible gas under pressure ignition means and valve means for controlling the flow of oxidizing atmosphere and combustible gas into the chamber.
- 25 14. A process according to claim 10 wherein the pulsed combustion has a frequency in the range of from 1 Hz to 20000 Hz.
- 30 15. A method according to claim 12 wherein the frequency is in the range of from 20 Hz to 1000 Hz.

16. A process according to claim 1 wherein the surface of the substrate is oxidized to provide functional groups and wherein the modifying agent is reactive with said functional groups.

5 17. A process according to claim 13 wherein the substrate is oxidized by oxidation means selected from the group consisting of corona discharge, plasma treatment, chemical oxidation, UV treatment and combustion in the presence of an oxidizing atmosphere.

10 18. A process according to claim 14 wherein said oxidation is conducted by means of combustion simultaneously with treatment of the substrate with the modifying agent.

15 19. A method according to claim 9 wherein the natural polymeric material is oxidized prior to treatment with the modifying agent.

20 20. A process according to claim 2 further comprising treating the substrate with a physical field selected from the group consisting of an ultrasonic field, a microwave field, a radio-frequency field, heat in the range of from 50 to 150°C and combinations of two or more thereof.

25 21. A process according to claim 1 wherein the modifying agent is selected from the group consisting of organo-titanates, organo-silanes and organo-zirconates.

30 22. A process according to claim 18 wherein the modifying agent is of formula X_aSiY_b , wherein X is a non-hydrolyzable organo-functional alkyl group, Y is a hydrolysable group, a is an integer from 1 to 3, and b is 4-a. In a particularly preferred group the organofunctional silane has the structure $X_aSi(OR)_b$ where X is a non-hydrolyzable organofunctional group bonded to silicone through a stable covalent bond, R is any suitable alkyl group, preferably methyl or ethyl, a is an integer from 1 to 3 and b is 4-a. The silanol groups obtained after hydrolysis of the alkoxy groups may react with the hydroxyl and/or other functional groups introduced onto the surface of the polymer.

23. A process according to claim 1 wherein the modifying agent is a multifunctional amine containing compound selected from the group consisting of: C₂ to C₃₆ linear, branched or cyclic compounds containing two or more amine groups; polymers of a number average molecular weight of from 300 to 3 million containing a multiplicity of amine group; C₂ to C₃₆ perfluoroamines; C₂ to C₃₆ amino alcohols/phenols; C₂ to C₃₆ amino acids; C₂ to C₃₆ amino aldehydes/ketone; C₂ to C₃₆ amino amides; C₂ to C₃₆ amino ethers; C₂ to C₃₆ amino esters; C₂ to C₃₆ amino nitros; C₂ to C₃₆ amino nitriles; C₂ to C₃₆ amino phosphoric acids; C₂ to C₃₆ amino sulfonic acids; C₂ to C₃₆ amino halogens; C₂ to C₃₆ amino alkenes; C₂ to C₃₆ amino alkynes; polymers of a number average molecular weight of from 300 to 3 million containing a multiplicity of amine groups and non-amine functional groups: amino polysaccharides, etc.
24. A process according to claim 2 wherein the surface modifying agent is a polyamine containing at least four amine groups including at least two amine groups selected from primary and secondary amine groups.
25. A process according to claim 4 wherein the polyamine compound is selected from the group consisting of polyamine polymers of molecular weight in the range of from 200 to 2000000 and non-polymeric polymers containing from 6 to 30 carbon atoms.
26. A process according to claim 24 wherein the polyamine is selected from the group consisting of polyamino polymers homopolymers containing the monomers, ethylenimine, allylamine, vinylamine, 4-aminostyrene, aminated acrylate/methacrylate, or as copolymers made from a combination of these monomers or as a copolymers containing at least one of these amine containing monomers with a non-amine monomer of the type ethylene, propylene, acrylate/methacrylate, ethylene oxide or a non-polymeric compound selected from the group consisting of triethylene tetraamine, tris(2-aminoethyl)amine, tetraethylene pentaamine, pentaethylene hexamine and benzene tetraamine.

27. A process according to claim 24 wherein the polyamine is a polyethylenimine, polyvinylamine or polyallylamine of molecular weight of from 400 to 750000.

5 28. A process according to claim 2 wherein the substrate is a cellulosic material derived from perennial plants.

29. A process according to claim 28 wherein the cellulosic material is selected from the group consisting of hardwood, softwood, cotton, jute, flax,
10 hemp, ramie, sisal, coir, viscose, softwood kraft and composites containing cellulose fibre.

30. A process according to claim 2 wherein concentration of the surface modifying agent in the solvent is in the range of from 0.00001 to 50% by
15 weight.

31. A process according to claim 30 wherein the concentration of the modifying agent is in the range of from 0.01 to 5% by weight.

20 32. A process according to claim 2 wherein the modifying agent is a solution in a solvent selected from the group consisting of aqueous solvents and alcohols.

33. A process according to claim 24 wherein the process further comprises
25 reacting the surface of the substrate with a cross-linking agent reactive with the polyamine to provide a cross-linked network grafted to the surface of the substrate.

34. A process according to claim 33 wherein the crosslinking agent has at
30 least two functional groups including a first functional group reactive with an amino functional group of the polyamine and a second functional group reactive with a functional group present in the polyamine or crosslinking agent.

35. A method according to claim 33 wherein the crosslinking agent is selected from the group consisting of organo-functional silanes having an organic functional group for reaction with an amine and a silane group adapted to condense with other silane groups in the presence of water to form Si-O-Si bonds; alcohol condensation reagents and products thereof; methylol crosslinkers; crosslinkers containing at least two oxirane groups; compounds containing at least one oxirane group and at least one acrylate or methacrylate group; compounds containing at least two groups independently selected from acrylate methacrylate methacrylamide/acrylamide, compounds containing one or more halogen groups and one or more groups selected from the group consisting of oxirane, methacrylate, acrylate, aldehyde, ketone, isocyanate and anhydride; compounds containing halohydrin and another functional group selected from the group consisting of oxirane, acrylate and methacrylate; and compounds containing at least two anhydride groups.

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36. A method according to claim 33 wherein the crosslinking agent is a silane of formula:



wherein

20 X is any organic fragment of from 3 to 60 carbon atoms containing at least one group selected from the group consisting of oxirane, anhydride, acid chloride, chloroformate, sulfonyl chloride, ketone, aldehyde, carboxyl, isocyanate, acrylate, methacrylate, acrylamide and alkyl halide;

R¹ is a group susceptible to hydrolysis; and

25 R² are independently selected from groups susceptible to hydrolysis and the group alkyl, aryl, vinyl, substituted alkyl substituted aryl and substituted vinyl.

37. A method according to claim 36 wherein the silane is of formula



30 wherein

R⁴ is a group of formula C_nH_{2n} wherein n is from 0 to 12 or a benzyl group of formula CH₂C₆H₄;

Y is selected from the group consisting of methacryloxy, acryloxy, acetoxy, halogen, carbomethoxy, 4-chlorosulfonylphenyl, isocyanate, chloroformate, carbochloride, 3,4-epoxycyclohexyl and ureido;

5 R^2 is selected from the group consisting of chloro, C_1 to C_{12} alkoxy and carboxylate of formula $O_2CC_nH_{2n+1}$ wherein n is an integer from 1 to 11; and

R^3 is selected from the group consisting of chloro, C_1 to C_{12} alkoxy, phenyl, cyclohexyl, cyclopentyl, C_1 to C_{12} alkyl, and carboxylate of formula $O_2CC_nH_{2n+1}$ wherein n is an integer from 1 to 11.

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38. A method according to claim 33 wherein the crosslinking agent is selected from:

aldol condensation products selected from the group consisting of glutaraldehyde, methyl pyruvate, ethylpyruvate, pyruvic aldehyde, methyl
15 levunate, ethyl levunate and mixtures of at least one of formaldehyde, glyoxal and glutaraldehyde with one or more ketone of formula $C_nH_{2n+1}CO$ C_mH_{2m+1} wherein n and m are independently selected from 0 to 6;

methylol crosslinkers provided by reaction of two or more molar equivalents of formaldehyde with at least one compound selected from the
20 group consisting of phenol or substituted phenol, melamine, urea, benzoguanamine and glucouril;

oxiranes selected from the group consisting of bisphenol A epoxy resins; di and poly glycidyl ethers of diols and polyols; glycidyl esters of polycarboxylic acids; di or poly glycidyl aliphatic or aromatic amines; epoxy compounds
25 obtained from peroxidation of unsaturated compounds; homo and copolymers of glycidyl methacrylate; homo and copolymers of glycidyl acrylate; epoxy acrylate compounds and epoxy methacrylate compounds;

polyunsaturated compounds selected from the group consisting of 2-(acryloxy)ethermethacrylate; ethoxylated bisphenol A di(meth)acrylate;
30 polyethylene glycol di(meth)acrylate; 1,3-butylene glycol di(meth)acrylate; propoxylated neopentyl glycol di(meth)acrylate; alkoxyated aliphatic di(meth)acrylate ester; tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate; pentaerythritol tri(meth)acrylate; glycerol propoxylate tri(meth)acrylate; pentaerythritol tetra(meth)acrylate; dipentaerythritol penta(meth)acrylate; di or

tri (meth)acrylate methacrylate ester; di or tri (meth)acrylate acrylate ester; aliphatic urethane (meth)acrylate and aromatic urethane (meth)acrylate;

halogen containing compounds selected from the group consisting of epichlorohydrin, epibromohydrin, epiiodohydrin; 2-bromoethyl acrylate; 3-bromopropyl acrylate; 4-bromobutyl acrylate; 6-bromohexyl acrylate; 7-bromoheptyl acrylate; 8-bromooctyl acrylate; 9-bromononyl acrylate; 11-bromoundecyl acrylate; 12-bromododecyl acrylate; 2-chloroethyl acrylate; 2-(2-chloroethoxy) ethyl acrylate; 2-[2-(2-chloroethoxy)ethoxy]ethyl acrylate; 4-chlorobutyl acrylate; 2-chlorocyclohexyl acrylate; 10-chlorodecyl acrylate; 6-chlorohexyl acrylate; 3-chloro-2,2-dimethylpropyl acrylate; 1-chloro-2-methyl-2-propyl acrylate; 8-chlorooctyl acrylate; 3-chloropropyl acrylate; 2-bromoethyl isocyanate; 2-chloroethyl isocyanate; ; 4-chlorobutyl isocyanate and trichloroacetyl isocyanate;

compounds containing at least one halohydrin group and at least one group selected from the group consisting of oxirane, acrylate, methacrylate and aldehyde linked to the halohydrin group by a hydrocarbon linking group; and

compounds containing two or more anhydride groups selected from the group consisting of pyromellitic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 3,4,9,10-perylenetetracarboxylic dianhydride and polymers containing maleic anhydride.

39. A method according to claim 33 wherein the weight ratio of polyamine to crosslinking agent is in the range of from 1:100 to 100:1.

40. A process according to claim 33 wherein the weight ratio of polyamine to crosslinking agent is in the range of from 1:10 to 10:1.

41. A process according to claim 33 wherein at least one of the modifying agent and crosslinking agent includes a functional group selected from the group consisting of electroconductive groups UV absorbing groups, IR absorbing groups, charge containing groups, ion exchange groups.

42. A method according to claim 2 wherein the method further includes the step of contacting treated substrate with a further material selected from the group consisting of an adhesive, functional molecules, coatings and inks.

- 5 43. A method according to claim 34 wherein the treated polysaccharide based material is contacted with a coating is selected from the group consisting of an ink, paint, varnish, lacquer, metallic coating, inorganic oxide coating, conductive or magnetic coating, bio-functional coating, linear or non-linear
10 optical coating, hard coating, UV-vis, IR, MW or RF absorbing or reflective coating, barrier coating and permeable coating.